Direct determination of Al content in molecular-beam epitaxially grown $Al_xGa_{1-x}As$ ($0 \leqslant x \leqslant 1$) by nuclear resonant reaction analysis and x-ray rocking curve techniques

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The techniques of nuclear resonant reaction analysis (NRRA) using $^{27}Al(p,\gamma)^{28}Si$ and x-ray rocking curve (XRC) based on double-crystal diffractometry have been utilized to determine directly the Al concentration and its depth distribution in molecular-beam epitaxially (MBE) grown $Al_xGa_{1-x}As$/GaAs heterojunctions. Combination of these two methods has revealed a linear relationship between the Al mole fraction and the lattice strain. This can eliminate the need for assuming that Vegard's law holds and that extrapolated elastic coefficients are accurate. The result supports that both of these techniques provide an accurate determination of the absolute Al content and crystalline quality in $Al_xGa_{1-x}As$/GaAs throughout the entire composition range ($0 \leqslant x \leqslant 1$) as well as profiling the Al distribution. In addition, significant depth fluctuations in the Al mole fraction in some samples have been probed by the NRRA technique as well as by the XRC. The result suggests that a reliable and accurate measurement must be undertaken to ensure the control of the required Al distribution, which is necessary for the high performance of many devices.

I. INTRODUCTION

$Al_xGa_{1-x}As$ is a very important alloy used in high-performance electronic and optical devices. In many of these structures the Al mode fraction plays a very crucial role with respect to eventual device performance. Specifically, the confinement of the optical field in low threshold, graded index, separate confinement GRINSCH lasers is strongly dependent on the exact Al profile,[1] which if not carefully controlled can lead to inferior performance. This is also true for modulation doped field effect transistors (MODFET's) where the Al mode fraction plays an important role in determining the current level.

The Al mole fraction in $Al_xGa_{1-x}As$ is commonly determined by analytical tools, e.g., secondary ion mass spectroscopy (SIMS) or Auger electron spectroscopy (AES). If the energy band gap versus the mole fraction and lattice constant versus the mole fraction are known, photoluminescence (PL), photoreflectance (PR), and x-ray techniques can also be used, respectively, provided that the mole fraction in the layer is constant or changes in noticeable steps. In the case of molecular-beam epitaxy (MBE) growth, the Al mole fraction is dependent on the Al flux which, in turn, is determined by the effusion cell temperature. It is often assumed that the depth distribution of the Al mole fraction is fairly flat unless deliberately modified, and that there are no unintentional gradients in its distribution. Only in very thin films are the flux transients, caused by shutter operation, considered.

The analytical tools mentioned above can also be used to determine the Al distribution in the direction of growth. The accuracy of these analytical techniques are, in many cases, not sufficient. For instance, the determination by photoluminescence is based on the accurate knowledge of the band gap as a function of the Al content.[2] However, recent results of PR, PL, NRRA, and microprobe analysis obtained by University of Illinois/Caltech,[3] IBM/Brooklyn College of CUNY,[4] and East Germany[5] teams indicate unequivocally that the old Dingle rule with considerable bowing does not hold in relating the band gap of $Al_xGa_{1-x}As$ to the mole fraction. The new expression is $E_g = 1.42 + 1.427x + 0.041x^2$. Note that the new slope ($1.427x$) is much steeper than the previewing reported. In addition, the direct–indirect crossover takes place at $x \sim 0.41$ at 300 K and $x \sim 0.37$ at 2 K. Therefore, a careful study and direct determination of Al depth fluctuation are required in order to gain insight and good understanding of the processes involved.

In this study, the nondestructive technique of nuclear resonant reaction analysis (NRRA) utilizing MeV protons with the sharp $^{27}Al(p,\gamma)^{28}Si$ resonant reaction has been employed. This technique, which has a depth resolution in the several tens of nm range near the surface, has revealed the fluctuation of Al mole fraction in some of the $Al_xGa_{1-x}As$ samples. The samples were also examined by the x-ray rocking curve (XRC) technique, through which the relative lattice strain and variation of lattice constant in the epilayer with respect to the substrate crystal were measured. The XRC results together with NRRA measurements have led to the production of a linear relationship between the lattice strain and Al mole fraction in $Al_xGa_{1-x}As$/GaAs heterojunctions. With this calibration curve, then, the XRC provides a sensitive technique to determine accurately the Al content in $Al_xGa_{1-x}As$/GaAs throughout the entire composition range ($0 \leqslant x \leqslant 1$).

II. EXPERIMENT

A. Sample preparation

The $Al_xGa_{1-x}As$/GaAs samples used in this study were grown on (100) GaAs substrates following standard MBE procedures. The typical growth sequence consisted of a 0.2-μm GaAs buffer layer followed by the desired ternary alloy. The $Al_xGa_{1-x}As$ epilayers, most of which were nominally

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undoped, range in thickness from 1 to 3 μm. In one series, the alloy composition was varied over the entire range between the two end binaries. In another series, the effect of substrate temperature and cell temperature controller was investigated in an effort to determine the role of the Al migration rate and the temperature control system on the depth fluctuation observed in some samples. An AlAs sample was used as a reference to convert the NRRA yield to the AlAs mole fraction and to obtain the strain field in $Al_xGa_{1-x}As$ for $x = 1$.

B. Depth profiling by the NRRA technique

The NRRA technique is a relatively nondestructive analytical method providing direct analysis of elemental concentration versus depth. Its principle has been described elsewhere[6–8] and will not be discussed here in detail. In brief, its use in elemental analysis and depth profiling depends on the existence of an isolated δ-function-like resonance in the nuclear reaction involving the appropriate isotope to be analyzed. Al depth profiling makes use of the nuclear $^{27}Al(p,\gamma)^{28}Si$ which has a very narrow isolated resonance at at a proton energy E_{lab} of 992 keV with a resonance width Γ of about 100 eV. In the measurement the sample is bombarded with protons in an appropriate energy range higher than the resonance energy, and the characteristic 10.7 MeV γ rays emitted during the reaction are detected. The γ-ray yield per incident ion is proportional to the amount of Al at the depth where the reactions occur. Selection of the incident proton energy is equivalent to specifying the depth at which the Al concentration is to be determined since the incident ion loses part of its kinetic energy down to the required resonant energy when it penetrates a certain depth in the target. Thus, γ-ray production measured versus the incident beam energy gives a direct measurement of Al concentration as a function of depth in the sample.

Our analysis is conducted with the Caltech EN-Tandem accelerator, and the experimental setup is similar to that described in Ref. 3 for hydrogen depth profiling. The samples were mounted in a special small glass chamber at the end of the beamline maintained under a vaccum of 5×10^{-6} Torr. The beam was focused and directed through a 1-mm-diam collimator normally onto the target with a current of about 30–50 nA. A 20×15 cm NaI(Tl) scintillation detector, placed at 90° to the incident beam direction, was used for γ-ray detection. During the measurement the incident proton beam energy was varied to generate the Al depth profile. At each point the γ-ray yield was taken from an energy window of the γ-ray spectrum. Conversion of the incident beam energy to depth scale in the target was made using the stopping cross section dE/dx which can be found in standard references.[9] The interpretation of the yield data as a function of the incident beam energy to the Al concentration versus the depth was made with the aid of a calibration constant which was obtained from a measurement of an AlAs sample, after correcting for the energy-loss differences of incident beam in the various target materials.

C. Strain measurement by the XRC technique

The XRC technique based on double-crystal diffractometry is a sensitive tool for the crystal structure analysis, such as atomic-deformation-induced strain and damage as well as lateral variations in crystals.[10,11] The XRC gives the reflecting power of the sample versus deviation of the incident angle from the Bragg angle. Both strain and misorientation cause an angular shift in the Bragg peak, while both the thickness of the strained layer and damage or defects, which change the structure factor, affect the integrated intensity and width of the Bragg peak. In a heterojunction system the lattice mismatch at the interface induces strain, while in a ternary alloy any change in elemental composition varies the lattice constant. Both of these will cause the Bragg angle to shift; thus, the XRC can be appropriately applied to ternary alloys for analyzing the mole fraction as well as for checking the crystalline quality. For the reflection from a well oriented crystal, the angular shift of the Bragg peak $\Delta\theta$ corresponds to the strain ϵ as $\epsilon = \Delta d/d = -\cot\Theta_B\Delta\theta$, where d and Δd are the lattice spacing and the corresponding deviation induced by strain in the direction of the reflection planes.

Our measurement was carried with the XRC system in Caltech Materials Science Laboratory. A highly monochromatic and planar Fe-$K\alpha_1$ x ray is incident onto the sample at the Bragg angle for (400) symmetrical diffraction with respect to the GaAs substrate, by which the perpendicular strain is measured. The sample is mounted on a goniometer which rotates the sample crystal step by step with a high precision of up to one ten-thousandths of a degree at a time. At each step the reflection intensity is acquired and recorded by a computerized data system. During data analysis, each reflection peak is numerically fitted with a Gaussian function by the least-square method to locate the center of the peak precisely, where the Bragg reflection peaks from the GaAs substrate are centered at the zero point as a reference. The angular shift between the strain peak and the reference peak is used to calculate the strain, which in turn leads to the Al mole fraction through the calibration constant from the linear correlation between the lattice strain and the Al mole fraction. The width of $Al_xGa_{1-x}As$ strain peak is obtained for evaluating crystalline quality.

III. RESULTS AND DISCUSSIONS

An AlAs sample was first used to determine the necessary yield calibration constants for mole fraction in the NRRA and the strain field in AlAs epilayer ($x = 1$) by the XRC. Note that by the NRRA, the Al concentration as well as the thickness of the epilayer can be determined with high precision, surface depth resolution being about 200 Å in AlAs. Because the resonant width itself is very narrow (100 eV), the surface depth resolution broadening is mainly due to the beam energy resolution, thermal Doppler effect, and instrumental line shape.[6,12,13] However, it is shown that the NRRA is quite sufficient for depth profiling as well as concentration analysis. In the XRC, the $Al_xGa_{1-x}As$ peak is found to have a negative angular shift, which indicates, as expected, that a larger lattice constant of AlAs and positive perpendicular elastic strains exist with respect to the GaAs substrate.

A. Al mole fraction versus lattice strain

The Al mole fraction can be determined by the normal x-ray technique on the assumption of Vegard's law which indi-

cates the linear correlation of the lattice constant with the mole fraction. But accurate measurement of the lattice constant is rather difficult as there always exists lattice-mismatch-induced strain in $Al_xGa_{1-x}As/GaAs$ heterojunctions. However, the XRC can measure the lattice strain very accurately, down to $10^{-5}\%$. Combination of XRC and NRRA can be used to relate the lattice strain in the film to the mole fraction of the $Al_xGa_{1-x}As$ layer. A set of $Al_xGa_{1-x}As/GaAs$ samples, covering the entire composition range, were analyzed for this purpose. The results show that the Al depth distribution in these samples is rather flat, and the reflection peak associated with $Al_xGa_{1-x}As$ in the rocking curves is sharp and singular. A summary of the results is shown in Fig. 1, where the strain in $Al_xGa_{1-x}As$ obtained from the XRC expressed in angular shift is plotted versus the Al mole fraction x established through the NRRA. One expected feature is that the measured strain field is larger than that strain estimated from the difference of relaxed lattice constants of individual alloys ($[a_{Al_xGa_{1-x}As} - a_{GaAs}]/a_{GaAs} \times 100\%$) which is about 0.14% at room temperature for AlAs–GaAs as reported earlier by Ettenberg and Paff.[14] This indicates that besides the lattice constant variation with the mole fraction, the elastic lattice-mismatch-induced strain exists due to differences in thermal expansion coefficients of $Al_xGa_{1-x}As$ and GaAs alloys. This closely agrees with the theoretical estimate[15] and the nature of the compressive strains.[14] It is found that a linear relationship between the lattice strain and Al mole fraction exists in $Al_xGa_{1-x}As/GaAs$ system with no exceptions. This implies that the strain field measurement using the highly sensitive XRC technique can lead to precise determination of the Al mole fraction as well as characterization of the crystalline quality of $Al_xGa_{1-x}As$ alloys.

B. Al depth fluctuation with growth condition

A set of samples were prepared under a variety of growth conditions as listed in Table I for checking the crystalline quality and depth distribution of the Al mole fraction. The depth profiles of Al concentration in these samples determined by NRRA are given in Fig. 2, and the corresponding XRC's are plotted in Fig. 3. The main features are summarized in Table I. First, significant fluctuations in the Al depth profile were observed in Sample #355 which was grown at 700 °C with the cell temperature controller. This modulation manifested itself in the XRC, as a cluster of several diffuse peaks, which closely agrees with the NRRA data. Note that these observations were limited to this sample only. When the epilayers were grown without the temperature controller under a constant power supply, at a substrate temperature of 600 °C (Sample #411) and 700 °C (Sample #418), they showed fairly flat Al depth distributions. The XRC data showed single and narrow diffraction peaks ($\delta\theta \simeq 0.013°$ for #411 and $\delta\theta \simeq 0.007°$ for #418). The results indicate that the quality of samples grown at high temperatures is better than those grown at low temperature. This is in agreement with MBE results reported earlier and those by Ettenberg and Paff[10] on the thermal expansion of AlAs. Based on their experiments they pointed out that in the epitaxial growth temperature ranging from 800 to 1000 °C there was almost a perfect lattice match. But a compromise has to be made since lattice strain will be introduced at the interface when the epitaxial layer is cooled down. The measurement has also shown the dependence of the distribution of the Al mole fraction on the stability of the cell temperature in MBE growth mode, which is of considerable importance for the fabrication of $Al_xGa_{1-x}As/GaAs$ heterojunction devices, and suggests that care should be exercised in MBE crystal growth.

TABLE I. Summary of the experimental results of $Al_xGa_{1-x}As$ samples grown by MBE under different conditions

Sample No.	Growth conditions: Temp.	Growth conditions: Controller	Depth profiles (by NRRA)	Lattice strains (by XRC)
355	High 700 °C	With	Big fluctuations	Double peaks overlapped with satellites
418	High 700 °C	Without	Flatter	Narrow peak with small satellites
459	Low 600 °C	With	Bad	Broadened peak with high background
411	Low 600 °C	Without	Good	Narrow peak with strong satellites

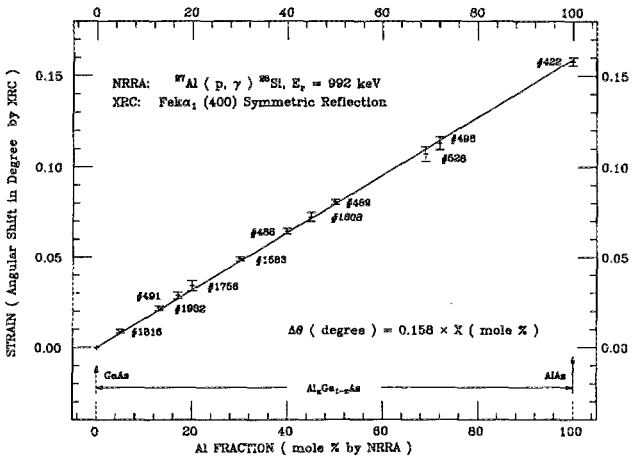

FIG. 1. Linear correlation between AlAs mole fraction and strain in MBE grown $Al_xGa_{1-x}As/GaAs$ heterojunction samples. The AlAs mole fractions were directly determined by the NRRA, and the strains were measured by the XRC in the (400) symmetric reflection.

IV. SUMMARY REMARKS

In summary, the Al mole fraction and depth distribution in MBE grown $Al_xGa_{1-x}As$ were studied by the nondestructive NRRA and XRC methods. Combination of these two techniques has led to a calibration curve giving a linear correlation between the experimentally determined lattice strain and the Al mole fraction over the entire composition range between GaAs and AlAs. Assuming coherent strain, the XRC measurement along with this calibration curve can be used to determine the Al mole fraction in the $Al_xGa_{1-x}As/GaAs$ heterojunctions. It should be pointed out that the XRC can also give us the information about Al

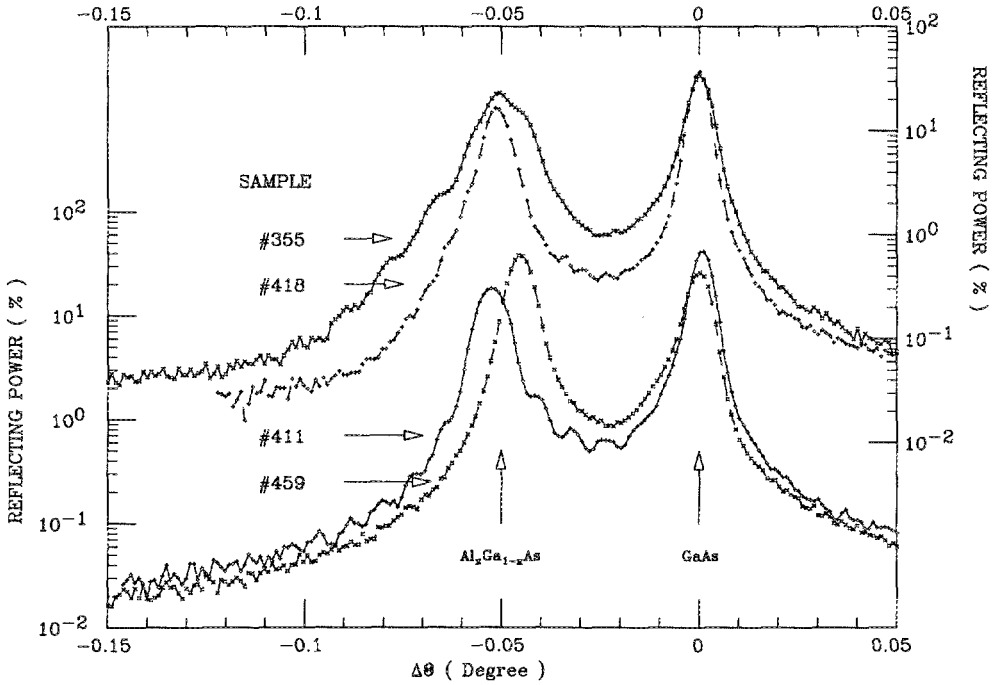

FIG. 2. ^{27}Al depth profiles of MBE grown $Al_xGa_{1-x}As/GaAs$ samples by the NRRA technique. The samples were prepared under different growth conditions as listed in Table I.

depth distribution. This can be done by employing the numerical simulation and fit to the experimental data with the x-ray diffraction kinematical and dynamical theories.[7] But its accuracy relies on primary knowledge of the possible strain distribution as a function of the Al depth distribution. Considering the lack of availability of NRRA facilities and the possible radiation damage induced during the analysis, the XRC may be preferred for the Al mole fraction determination once the strain versus the mole fraction curve is established through NRRA and XRC. However, the NRRA can profile the Al depth distribution as well as directly determine the Al concentration.

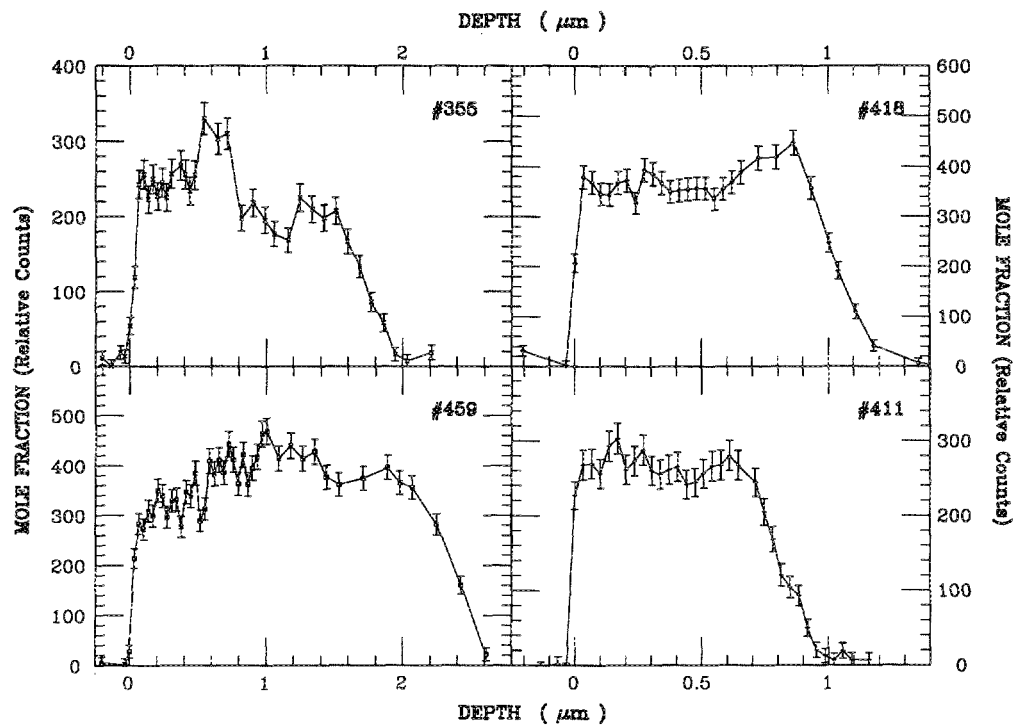

FIG. 3. XRC of the (400) symmetric reflection from MBE grown $Al_xGa_{1-x}As/GaAs$ samples prepared under different conditions.

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